

Citation for published version:

Garcia, L, Mahon, MF & Hill, MS 2019, 'Multimetallic Alkaline-Earth Hydride Cations', *Organometallics*, vol. 38, no. 19, pp. 3778-3785. <https://doi.org/10.1021/acs.organomet.9b00493>

DOI:

[10.1021/acs.organomet.9b00493](https://doi.org/10.1021/acs.organomet.9b00493)

Publication date:

2019

Document Version

Peer reviewed version

[Link to publication](#)

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Multimetallic Alkaline Earth Hydride Cations

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Abstract

Reactions of dimeric β -diketiminato (BDI) magnesium and calcium hydrides with $[(BDI)Mg]^+[Al\{OC(CF_3)_3\}_4]^-$ provide ionic multimetallic hydride derivatives, which have been characterized by single crystal X-ray diffraction analysis. The wholly magnesium-centered species comprises a cation in which two $[(BDI)Mg]^+$ units are connected by a single μ^2 -bridging hydride. In contrast, the greater lability of the calcium-containing system is underscored by the isolation of a cyclic heterotrimetallic species in which a CaH_2 moiety is coordinated by a molecule of benzene and an aryl substituent of a $\{[(BDI)Mg]_2H\}^+$ cation. The homometallic dimagnesium species displays a greater facility toward reaction with diphenylacetylene than neutral $[(BDI)MgH]_2$, albeit the resultant crystallographically characterized vinylmagnesium cation equilibrates into a complex mixture of neutral and ionic species in solution. An initial assessment of both systems for the hydrosilylation of 1-hexene and diphenylacetylene evidences an inferior catalytic performance to $[(BDI)MgH]_2$ in isolation.

Introduction

The chemistry of molecular saline hydrides has advanced significantly during the past decade.¹ Whereas the synthesis and structures of the first strontium and barium hydrides have only recently been established,²⁻⁶ a wide range of lighter magnesium and calcium species are now available for study such that a diverse and unique reaction chemistry is also starting to emerge.^{2, 7-35} The exploitation of β -diketiminato (BDI) derivatives such as compounds **1** – **4** (Chart 1) has been central to these latter advances, allowing the development of a wide range of novel stoichiometric and catalytic processes.³⁶⁻³⁹ The dimeric magnesium hydride (**1**) in particular has enabled a plethora of hydrosilylation and hydroboration chemistries. This reactivity, however, has been largely restricted to the reduction of heteroatom-containing $C=E$ (e.g. $E = O$,^{40, 41} NR ⁴²⁻⁴⁵) and $C\equiv E$ ($E = O$,^{46, 47} N ^{48, 49}) multiple bonds and, although the transition metal promoted addition of alkenes to MgH_2 has been described,⁵⁰⁻⁵⁴ definitive examples of the hydromagnesiation of less polarized carbon-carbon multiple bonds are more limited. The terminal Mg-H bonds of compounds **5** and **6** have been reported by the groups of Okuda and Parkin, respectively, to react with styrene.^{32, 35} Both of these reactions take place at room temperature and within minutes to yield either selective formation of the magnesium 1-phenylethyl (for **5**) or a mixture of the 1-phenylethyl and 2-phenylethyl (for **6**) derivatives. We have very recently observed that the dimeric BDI derivative **1** reacts similarly with a significant range of terminal n -alkenes, to provide access to the

corresponding halide-free magnesium organometallics.⁵⁵ Although this insertion reactivity also provided a basis for the catalytic hydrosilylation of a range of alkene substrates with PhSiH_3 , much of this chemistry was notably slow and many of the reactions required several days heating at 60 - 80 °C to achieve high (>90%) conversions.

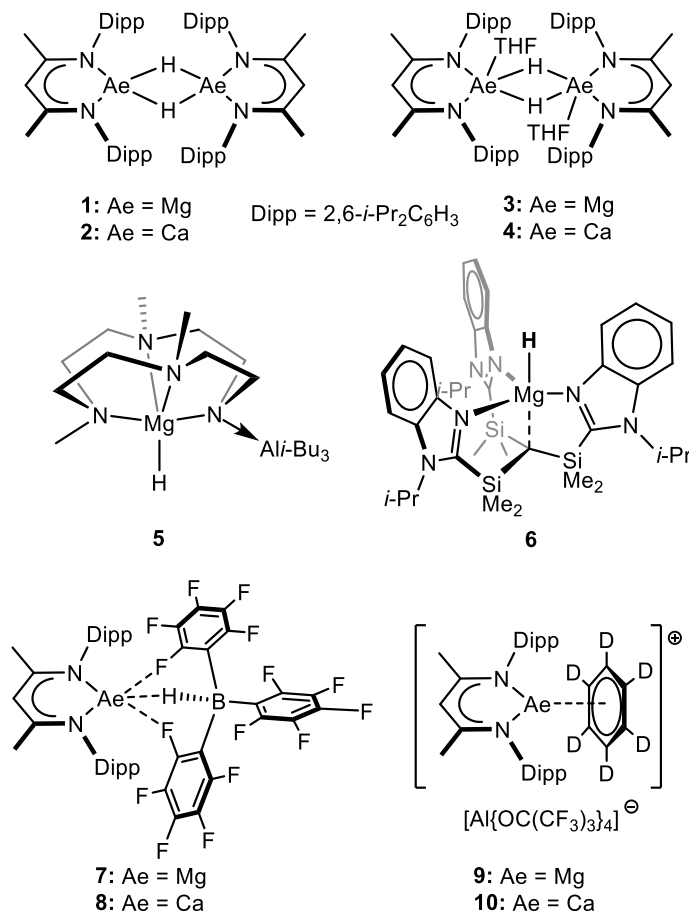


Chart 1: Previously reported magnesium and calcium compounds relevant to this study.

In related research, we have observed that the ability of BDI-supported magnesium and calcium hydride derivatives to effect the catalytic hydroboration of CO_2 and related heterocumulenes may be improved through the introduction of the Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$.^{56, 57} Although the catalytic action of the fluorinated borane could not be deduced with any degree of certainty, it was shown that compounds **7** and **8**, containing the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion, played a key role during catalytic turnover. The group of Okuda has also presented evidence that cationic Mg and Ca hydride species supported by tri- and tetra-aza macrocyclic ligands may display enhanced reactivity toward multiply bonded small molecules.^{13-15, 34} During a similar timeframe we have reported that use of the weakly coordinating anion, $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$, allows the isolation of $[(\text{BDI})\text{Ae}]^+$ cations, which are sufficiently electrophilic to permit the crystallization of charge separated alkaline earth $\eta^6\text{-}\pi$ adducts of benzene (e.g. **9**; Ae = Mg; **10**; Ca) and toluene.⁵⁸ Harder and co-workers' observations of closely related systems, in which identical $[(\text{BDI})\text{Ae}]^+$ cations are combined with $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, have led them to deduce that the Lewis

acidity of the resultant Mg and Ca centers is competitive with that of $B(C_6F_5)_3$.⁵⁹⁻⁶² Prompted by these observations plus the augmented reactivity of **7** and **8**, we, therefore, speculated that β -diketiminato magnesium and calcium hydride derivatives could be to be similarly activated toward a broader palette of polarized insertion reactivity through the introduction of a Lewis acidic $[(BDI)Mg]^+$ co-catalyst. In this contribution, we describe the successful characterization of the resultant ionic hydride species and provide an initial assessment of their utility as catalysts for the hydrosilylation of C-C multiple bonds.

Experimental Section

General considerations and starting materials

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J. Young tap NMR tubes prepared and sealed in a Glovebox. NMR spectra were recorded on a Bruker AV300 spectrometer operating at 300.2 MHz (1H) or an Agilent ProPulse spectrometer operating at 500 MHz (1H) and 470 MHz (^{19}F). The spectra were referenced relative to residual protio solvent resonances. C_6D_6 was purchased from Sigma-Aldrich Corp., dried over a potassium mirror before distilling under argon and storing over molecular sieves in the glovebox. Triphenylcarbenium tetrakis(perfluoro-*tert*-butoxy)aluminate ($[Ph_3C][Al(OC(CF_3)_3)_4]$) was purchased from Ionic Liquids Technologies GmbH and phenylsilane (97%) from Sigma-Aldrich Corp., both of which were used without further purification. Diphenylacetylene (98%) was purchased from Sigma-Aldrich Corp., recrystallized from ethanol and dried under high vacuum. 1-Hexene (97%) was purchased from Sigma-Aldrich Corp., dried over calcium hydride and distilled under argon before use. $[(BDI)MgH]_2$ (**1**), $[(BDI)CaH]_2$ (**2**) and $[(BDI)Mg(C_6D_6)][Al\{OC(CF_3)_3\}_4]$ (**9**) (BDI = $HC\{(Me)CN(Dipp)\}_2$; Dipp = 2,6-*i*-Pr $_2$ C $_6$ H $_3$) were synthesized by literature procedures.^{18, 23, 58} Microanalysis was performed by Mr. S. Boyer of London Metropolitan Enterprises.

Synthesis of compound 11

$[(BDI)Mg(C_6D_6)][Al\{OC(CF_3)_3\}_4]$ (**9**) (90 mg, 0.060 mmol) and $[(BDI)MgH]_2$ (**1**) (25 mg, 0.030 mmol) were dissolved in C_6D_6 (0.5 mL) in a sealed J. Young NMR tube, with the appearance of two immiscible phases. The resulting mixture was vigorously shaken for one minute and left overnight at room temperature. Colorless crystals of **11** suitable for X-ray analysis were formed by slow diffusion of hexane into the reaction mixture (87 mg, 78%). 1H NMR (500 MHz, C_6D_6 , 298K): δ 7.32 (m, 2H, *m*-CH Dipp), 7.06 (t, $^3J_{HH} = 7.7$ Hz, 4H, *p*-CH Dipp), 7.00 (m, 2H, *m*-CH Dipp), 6.92 (d, $^3J_{HH} = 7.7$ Hz, 4H, *m*-CH Dipp), 4.76 (s, 2H, $CH\{C(CH_3)NDipp\}_2$), 2.59 (sept, $^3J_{HH} = 6.9$ Hz, 8H, $CH(CH_3)_2$), 1.35 (s, 12H, $CH\{C(CH_3)NDipp\}_2$), 0.99 (d, $^3J_{HH} = 6.9$ Hz, 24H, $CH(CH_3)_2$), 0.61 ppm (d, $^3J_{HH} = 6.9$ Hz, 24H, $CH(CH_3)_2$). $^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6 , 298K): δ -74.83 ppm (s). Elemental analysis (%). Found: C 46.87, H 4.52, N 3.02. Calculated for $C_{74}H_{83}N_4Mg_2AlF_{36}O_4$: C 47.99, H 4.52, N 3.03.

Synthesis of compound 12

In a sealed J. Young NMR tube, [(BDI)Mg(C₆D₆)] [Al{OC(CF₃)₃}₄] (**9**) (90 mg, 0.060 mmol) and [(BDI)CaH]₂ (**2**) (28 mg, 0.030 mmol) were dissolved in C₆D₆ (0.5 mL), with the appearance of two immiscible phases. The resulting mixture was vigorously shaken for one minute and left overnight at room temperature. Colorless crystals of **12** along with crystals of [(BDI)Ca(C₆D₆)] [Al{OC(CF₃)₃}₄] (**10**) suitable for X-ray analysis were formed by slow diffusion of hexane into the reaction mixture. ¹H NMR (500 MHz, C₆D₆, 298K): δ 7.14 – 6.99 (12H, CH Dipp), 4.85 (s, 1H, CH{C(Me)NDipp}₂), 4.78 (s, 1H, CH{C(Me)NDipp}₂), 3.82 (s, 2H, CaH₂), 3.17 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 2.96 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 1.62 (s, 6H, CH{C(CH₃)NDipp}₂), 1.53 (s, 6H, CH{C(CH₃)NDipp}₂), 1.13 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.12 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.01 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.00 ppm (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂). ¹⁹F{¹H} NMR (470 MHz, C₆D₆, 298K): δ –74.81 ppm (s). The formation of the by-products [(BDI)MgH]₂, [(BDI)₂Ca] was also observed by ¹H NMR spectroscopy (see Figure S5).

Synthesis of compound 13

Compound **11** (30 mg, 0.016 mmol) and diphenylacetylene (2.9 mg, 0.016 mmol) were dissolved in C₆D₆ (0.5 mL) in a sealed J. Young NMR tube, with the appearance of two immiscible phases. The resulting mixture was vigorously shaken for one minute and left overnight at room temperature. Colorless crystals of **13** suitable for X-ray analysis were formed by slow diffusion of hexane into the reaction mixture. ¹H NMR (500 MHz, C₆D₆, 298K): δ 4.89 (s, 1H, CH{C(CH₃)NDipp}₂), 4.71 (broad s, 0.5H, CH{C(CH₃)NDipp}₂), 4.68 (s, 1H, PhCH), 2.68 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 2.50 (broad, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 1.46 (s, 6H, CH{C(CH₃)NDipp}₂), 1.09 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 0.91 (broad, 6H, CH(CH₃)₂), 0.71 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 0.53 ppm (broad, 6H, CH(CH₃)₂). ¹⁹F{¹H} NMR (470 MHz, C₆D₆, 298K): δ –74.81 ppm (s).

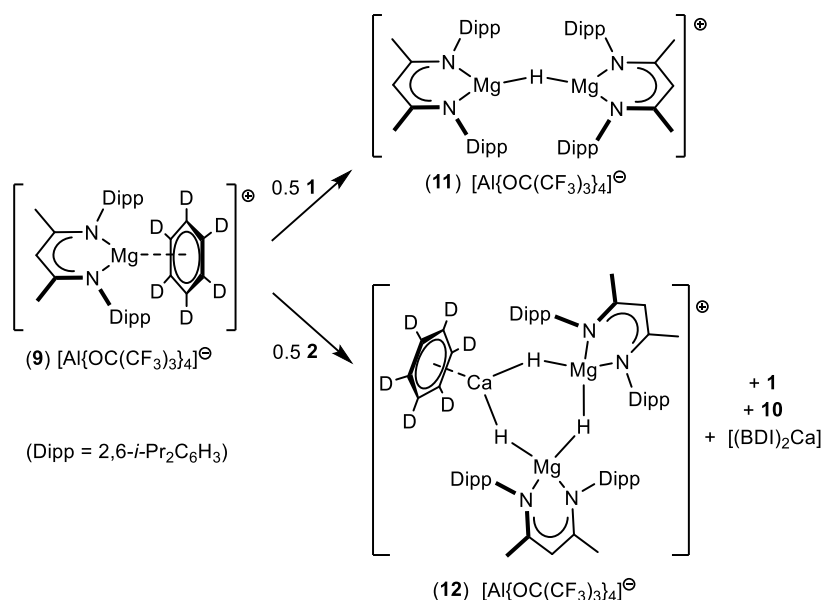
General method for catalytic hydrosilylation mediated by 11 and 12

In a J. Young NMR tube, compound **11** or **12** (generated *in situ*) (10 mol%), substrate (1-hexene or diphenylacetylene, 0.048 mmol) and phenylsilane (0.072 mmol) were dissolved in C₆D₆ (0.4 mL) and the resulting solutions heated at 60, 80 or 100 °C. The reactions were monitored by ¹H NMR spectroscopy with their progress evidenced by the consumption of substrate resonances alongside the emergence of the respective SiH₂ resonances of the *n*-hexyl- and 1,2-diphenylvinylsilane products.

Results and Discussion

Synthesis of multimetallic magnesium and calcium hydride cations. In common with our previous observations of the physical behavior of BDI-supported alkaline earth derivatives of the [Al{OC(CF₃)₃}₄][–] anion,⁵⁸ addition of two molar equivalents of the ionic magnesium species (**9**) to

compound **1** in benzene resulted in the immediate formation of a two phase system comprising an upper, more mobile solution and an oily lower phase, characteristic of liquid clathrate formation (Figure S3).⁶³ Although the initial ¹H NMR spectrum of this reaction mixture was broad and uninformative,⁶⁴ colorless crystals of the ionic dimagnesium hydride derivative (**11**) were grown by slow diffusion of *n*-hexane into the reaction mixture at room temperature (Scheme 1).



Scheme 1: Synthesis of compounds **11** and **12**.

Subsequent preparation of a more dilute sample of compound **11** in C₆D₆ enabled the acquisition of NMR data consistent with the formation of a single new BDI ligand environment. The resultant ¹H and ¹⁹F spectra did not allow definitive identification of the desired hydride species, however, analysis in the solid state by single crystal X-ray diffraction confirmed the identity of compound **11** as a charge-separated ion pair. Although the $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ anion was significantly disordered, the cationic component was unambiguously identified to comprise two $[(\text{BDI})\text{Mg}]^+$ units connected by a single μ^2 -bridging hydride, which was located and refined without restraints (Figure 1a).

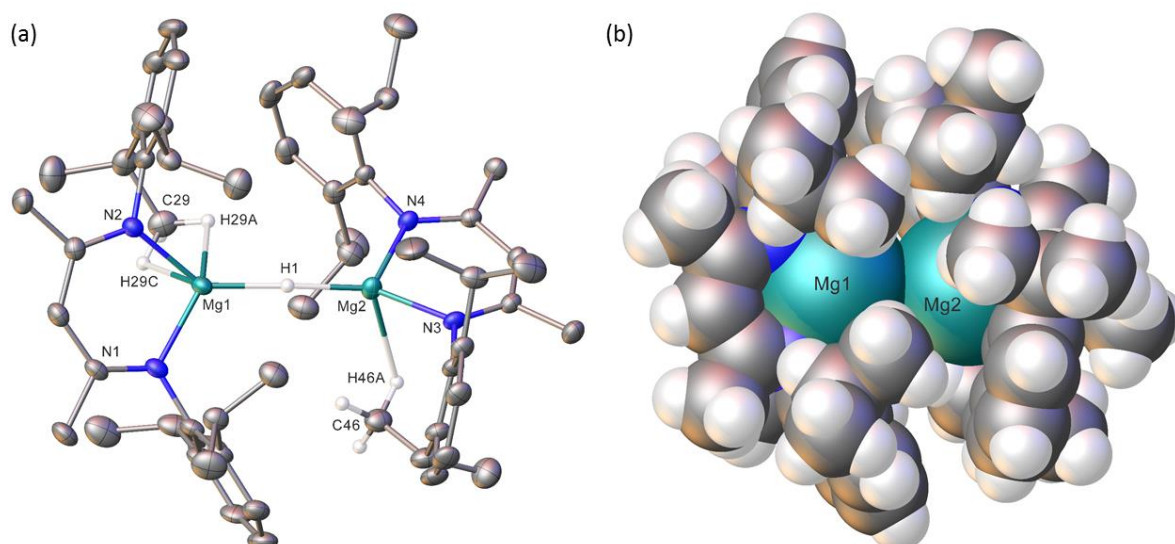


Figure 1: (a) ORTEP representation of the cationic component of compound **11** (30% probability ellipsoids). Hydrogen atoms apart from H1, H29A-C and H46A-C are removed for clarity. Selected bond lengths (Å) and angles (°): Mg1-N1 1.985(3), Mg1-N2 1.982(3), Mg2-N3 1.984(3), Mg2-N4 1.978(2), N1-Mg1-Mg2 119.00(9), N3-Mg2-N4 97.24(11); (b) space filling representation of compound **11**.

Both magnesium centers of the cationic component of compound **11** display distorted trigonal planar geometries defined by the bidentate BDI ligands and the bridging hydride. The coordination spheres of Mg1 and Mg2 are augmented, respectively, by close contacts with the C29- and C46-containing methyl groups of the 2,6-di-*iso*-propylphenyl substituents. The formal positive charge borne by the dimagnesium unit is reflected in the Mg-N contacts [ca. 1.98 Å], which are comparable to those observed in the monometallic cation, compound **9** [1.981(3), 1.971(3) Å],⁵⁸ and are significantly foreshortened relative to the analogous distances in the similarly dimeric but charge neutral μ^2 -H₂-bridged compound **1** [2.064(2), 2.065(2) Å].⁹ Although the effectively linear Mg-H-Mg (3.56°) linkage of **11** enforces a significant elongation of the Mg \cdots Mg separation [3.5719(14) Å] in comparison to that of compound **1** [2.890(2) Å], the high degree of steric protection provided to the magnesium-to-hydride bonds by the interdigitated BDI aryl substituents (dihedral angle subtended by the least-squares planes defined by the (BDI)Mg heterocycles = 47.27°) is clearly apparent from inspection of a space-filling model of the bimetallic cation (Figure 1b).

In an attempt to extend this synthetic protocol to the formation of heterobimetallic species, a further reaction was carried out in C₆D₆ between compound **9** and the solvent-free calcium hydride [(BDI)CaH]₂ (**2**) (Scheme 1). While this procedure also provided a two phase system, slow diffusion of *n*-hexane again yielded a crop of colorless crystals, which was identified as a mixture of a new compound (**12**) and the previously reported ionic calcium species, [(BDI)Ca(C₆D₆)]⁺ [Al{OC(CF₃)₃]₄]⁻ (**10**). Although this latter compound was readily identified by comparison with the previously reported

unit cell parameters, its presence hampered the isolation of an analytically pure bulk sample of compound **12**. Analysis by X-ray diffraction after mechanical separation of single crystals, however, enabled the identification of compound **12** as a further ionic aluminate derivative comprising a cyclic heterotrimetallic $[(\text{BDI})\text{Mg}]_2\text{Ca}(\text{C}_6\text{D}_6)\text{H}_3]^+$ cation (Figure 2a). Although several bimetallic hydride derivatives containing either sodium or potassium with magnesium have been described previously,^{25, 27, 65, 66} compound **12** appears to provide the first example of a well-defined molecular hydride containing two dissimilar group 2 elements. The cyclic $\{\text{Mg}_2\text{CaH}_3\}$ core of the cation is constructed about a unique μ -Mg-H-Mg interaction and two further μ^2 -H bridges, which connect the CaH_2 component with both magnesium centers of a $[(\text{BDI})\text{Mg}]_2\text{H}^+$ moiety. Although the BDI ligand of the cationic starting material **11** is retained at both Mg1 and Mg2, the coordination sphere of Ca1 is completed through η^6 -interactions with both the C47-C52-containing Dipp substituent of the Mg2-bound BDI ligand and a π -coordinated molecule of benzene solvent. The Ca-C distances to this latter ligand [range; 2.870(6) – 2.926(5) Å] are comparable to those observed in compound **10** [2.932(5) – 2.935(5) Å]. In this earlier case, π -back-donation from the benzene HOMO into an empty 3d orbital of the calcium center was computed to provide a modicum (ca. 8.5%) of the ligand to metal binding.⁵⁸ Although we have not carried out similar calculations in the current work, and the issue of *nd* orbital participation in main group species has long been a bone of contention,^{67, 68} the similarity of the Ca-C distances lead us to tentatively suggest that a similar bonding situation may prevail in compound **12**.

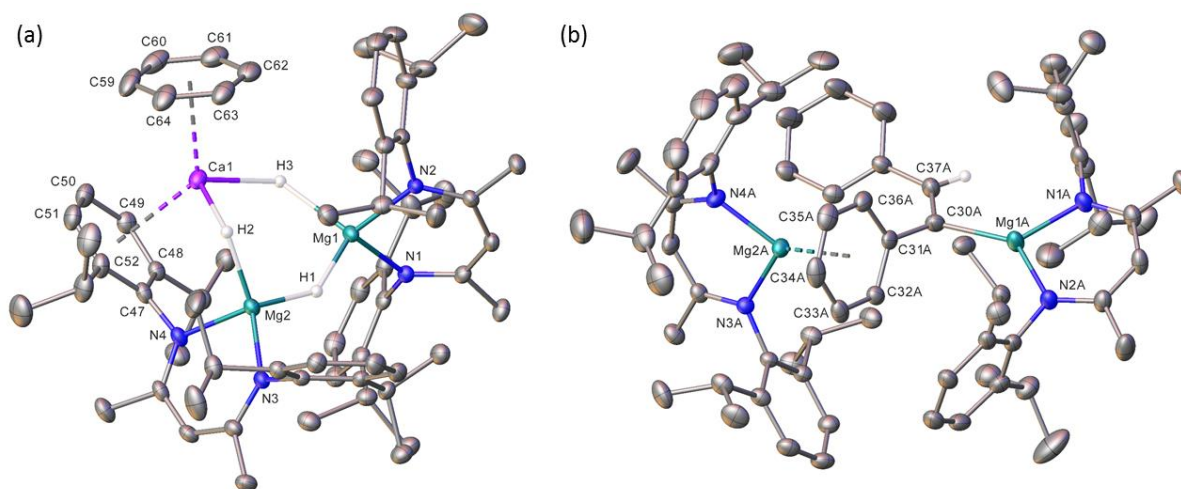


Figure 2: ORTEP representations (25% probability ellipsoids) of (a) the cationic component of compound **12** and (b) the Mg1A-containing cationic component of compound **13**. Hydrogen atoms apart from the bridging hydrides (H1-H3) of **12** and H37A of **13** are removed for clarity. Selected bond lengths (Å) and angles (°): (**12**) Mg1-N1 2.059(3), Mg1-N2 2.054(3), Mg2-N3 2.026(3), Mg2-N4 2.064(3), Ca1-C47 2.930(4), Ca1-C48 2.852(4), Ca1-C49 2.862(4), Ca1-C50 2.959(5), Ca1-C51 3.028(5), Ca1-C52 3.032(5), Ca1-C59 2.908(5), Ca1-C60 2.892(6), Ca1-C61 2.870(6), Ca1-C62 2.880(5), Ca1-C63 2.890(5), Ca1-C64 2.926(5), N2-Mg1-N1 93.99(13), N3-Mg2-N4 94.45(14); (**13**) Mg1-N1A 1.973(4), Mg1A-N2A 1.979(4), Mg1A-C30A 2.099(5), Mg2A-N3A 2.013(3), Mg2A-N4A

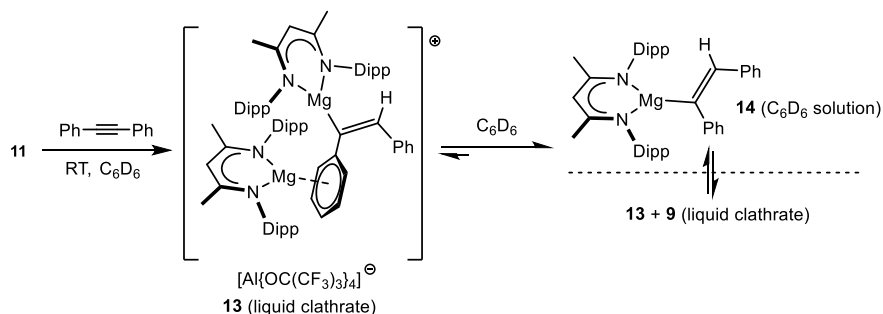
1.990(4), Mg2A-C31A 2.677(4), Mg2A-C32A 2.632(4), Mg2A-C33A 2.595(4), Mg2A-C34A 2.556(5), Mg2A-C35A 2.532(5), Mg2A-C36A 2.561(4), C30A-C37A 1.353(6), N1B-Mg1B-N2B 97.08(15), N1B-Mg1B-C32B 129.37(16), N2B-Mg1B-C32B 133.20(17), N4B-Mg2B-N3B 97.10(15).

Although detailed solution studies of the isolated mixture of crystalline compounds from this reaction were again hampered by phase separation into a liquid clathrate system, the resultant ^1H NMR spectrum in C_6D_6 provided tentative evidence for the retention of the asymmetric solid-state structure of **12**. In common with our previous observations,⁵⁸ no resonances attributable to the BDI ligand of the co-crystallized product **10** could be definitively identified by ^1H NMR spectroscopy. In contrast, two BDI ligand environments were clearly apparent from the observation of two discriminated ^1H BDI methine resonances at δ 4.79 and 4.85 ppm, which appeared alongside a further 2H singlet signal at δ 3.83 ppm ascribed to the two calcium-bound hydride ligands.

In common with previously reported calcium hydrides and other heteroleptic BDI derivatives of calcium,^{17, 18, 69} the absence of the bidentate ligand from Ca1 in the structure of **12** indicates that the species formed by the combination of compounds **2** and **9** in benzene are prey to facile solution equilibration. This deduction was supported by further solution study of the reaction between compounds **2** and **9** after 24 hours, at which point ^1H NMR spectroscopy provided evidence of the formation of a mixture of products (Figure S5), including compounds **12**, **1** and the known homoleptic calcium β -diketiminato, $[(\text{BDI})_2\text{Ca}]$.⁷⁰ While the observation of this latter species indicates the likely fate of the BDI ligand lost during the production of compound **12**, the generation of compounds **1** and **10** is consistent with the greater relative affinity of the Mg and Ca centers toward hydride and arene binding, respectively.

Reactivity of compound 11 with diphenylacetylene. Having confirmed the viability of this synthetic route to multimetallic hydride cations, we turned our attention to their stoichiometric and catalytic reactivity with unsaturated $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonded substrates. An initial reaction performed between compound **11** and diphenylacetylene in C_6D_6 at room temperature again resulted in the formation of two immiscible liquid phases. Analysis of this system by ^1H NMR spectroscopy provided evidence for the consumption of the acetylene starting material to afford a new species (**13**) comprising a 1,2-diphenylvinyl anion, characterized by the emergence of a sharp singlet resonance at δ 4.68 ppm. Although interpretation of the relative signal intensities was unreliable due to liquid clathrate formation, two further BDI methine resonances at δ 4.89 and 4.71 ppm were also tentatively identified to arise from **13**. Notably, and in common with several of the upfield multiplet and doublet resonances arising from the BDI *iso*-propyl substituents, the latter of these signals was significantly broadened while clear evidence for the continued presence of unreacted **11** was provided by the persistence of its BDI methine signal at δ 4.76 ppm. Despite the apparent complexity of this system, slow diffusion of hexane into the

reaction mixture provided a small crop of colorless single crystals of compound **13** suitable for X-ray diffraction analysis. The results of this analysis revealed the formation of a further charge separated species, the asymmetric unit of which comprised two aluminate anions and two bimetallic β -diketiminato (*E*)-1,2-diphenylvinylmagnesium cations (Figure 2b), the formal product of reductive $C\equiv C$ insertion into a Mg-H bond of the bimetallic cation of compound **11**. Although both anions were again heavily disordered, disorder in the cations was confined to one isopropyl group in each case. As both cations are largely similar, only the Mg1A/2A-containing component will be discussed herein. The reaction between **13** and diphenylacetylene results in *syn* addition of the Mg-H bond to provide an otherwise unperturbed vinyl anion [C30A-C37A 1.353(6) Å], which displays conventional κ^1 -binding of the three-coordinate Mg1A center [Mg1A-C30A 2.099(5) Å]. In contrast, Mg2A interacts in a η^6 -fashion with the 1-phenyl (C31A-C36A) substituent of the vinyl substituent. The resultant Mg-C distances [range, 2.532(5) - 2.677(4) Å] are reminiscent of the magnesium-to-benzene bonds observed in the cationic [(BDI)Mg(C₆D₆)]⁺ component of compound **9** [2.507(6) - 2.611(6) Å].⁵⁸ These observations lead us to suggest that the bimetallic component of compound **13** is best viewed as a η^6 -adduct of a [(BDI)Mg]⁺ cation and the neutral β -diketiminato (*E*)-(1,2-diphenylvinyl)magnesium species, [(BDI)Mg{(E)-CPh=C(H)Ph}] (**14**),⁵⁵ and that the assembly of compound **13** is primarily a solid state phenomenon. This latter deduction was supported by a further reaction of compound **11** and diphenylacetylene from which the upper, more mobile and solvent-rich phase was decanted after separation into the two liquid phases. Subsequent removal of volatiles provided a solid material that yielded a ¹H NMR spectrum, the major component of which could be assigned to [(BDI)Mg{(E)-CPh=C(H)Ph}] (**14**).⁵⁵ High conversions of this latter compound by the direct reaction of compound **1** and diphenylacetylene were only achieved after long reaction times (>5 days) and at elevated temperature (80 °C).⁵⁵ The less energetic conditions required for the reaction between **11** and diphenylacetylene imply, therefore, that the insertion process is facilitated by its cationic constitution, albeit the resultant species is labile in benzene solution towards the partitioning of [(BDI)Mg(C₆D₆)]⁺ [Al{OC(CF₃)₃}₄]⁻ (**9**) into the more viscous liquid clathrate phase (Scheme 2).



Scheme 2: Synthesis of compound **13** and its clathrate-induced equilibration to compounds **9** and **14** in C₆D₆ solution.

Catalytic hydrosilylation of diphenylacetylene and 1-hexene mediated by compounds **11** and **12**.

With these observations in hand, we assayed the ability of compounds **11** and **12** to effect the catalytic hydrosilylation of diphenylacetylene and 1-hexene with PhSiH₃. We have recently reported that both of these reactions may be successfully catalyzed by **1** to >95% conversions into the hexyl- and 1,2-diphenylvinylsilane products at temperatures >60 °C, albeit reaction times of ca. one month were required for high conversion of diphenylacetylene. For comparative purposes, those data are repeated in Table 1,⁵⁵ which also summarizes the outcome of analogous reactions performed with similar 10 mol% catalytic loadings of compounds **11** and **12**. Reactions were performed in C₆D₆ and were monitored by ¹H NMR spectroscopy by the consumption of substrate resonances alongside the emergence of the respective SiH₂ resonances of the hexyl- and vinylsilane products.

Table 1: Catalytic hydrosilylation of 1-hexene and diphenylacetylene mediated by **1**, **11** and **12** (10%, C₆D₆).

Entry	Substrate	Product	Catalyst	T °C	<i>t</i> (days)	% Conv.
1			1	60	7	97
				80	4	99
			11	100	3	23
					4	26
					7	29
					14	30
2			1	80	30	95
			11	100	3	0
3			1	80	4	99
			12	80	3	12
4			1	60	14	16
				80	30	95
			12	40	5	71

Examination of entries 1 and 2 in Table 1 confirms that compound **11** is significantly outperformed by compound **1**, even with the application of a more elevated temperature. The catalytic activity of **11** for the hydrosilylation of 1-hexene was also observed to decrease with continued heating until any discernible evidence of continued catalysis had ceased after 14 days at 100 °C (entry 1 and Figure S11). Similarly, although compound **13** was observed to form during the early stages of the reaction with diphenylacetylene, no evidence for onward catalysis or consumption of the silane reagent was observed (entry 2 and Figure S12). The reactivity of compound **12** for the conversion of 1-hexene was also disappointing and, although the mode of conversion is obscure, any catalysis was effectively limited to a single turnover (entry 3), possibly through catalyst depletion by redistribution to form [(BDI)₂Ca] (see Figures S13 and S14). In a similar manner, although the hydrosilylation of diphenylacetylene was catalyzed by **12** under milder conditions (40 °C) than those required by compound **1** (entry 4),

conversion to the vinylsilane was limited to 71% and ceased completely after 5 days due to the formation of $[(\text{BDI})_2\text{Ca}]$ (see Figure S15).

Conclusion

Reactions of β -diketiminato magnesium and calcium hydrides with a β -diketiminato magnesium cation paired with the weakly coordinating anion, $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$, provide access to ionic multimetallic hydride derivatives. Although their solution characterization was hampered by phase separation typical of liquid clathrate formation, the solid-state structures of both resultant species have been identified by single crystal X-ray diffraction analysis. The greater lability of the calcium derivative is underscored by the isolation of a trimetallic species in which the dihydrido heavier alkaline earth center is coordinated by an aryl substituent of a magnesium-coordinated BDI ligand and a molecule of benzene. The homometallic dimagnesium species displays a greater facility toward reaction with diphenylacetylene than neutral $[(\text{BDI})\text{MgH}]_2$, albeit the resultant isolable ionic vinylmagnesium complex equilibrates into a complex mixture of neutral and ionic species, which are again partitioned between two liquid/solution phases. While this enhanced polarized insertion reactivity might suggest that these compounds should also display improved performance in catalysis, this is not borne out by an initial assessment of their use for the hydrosilylation of 1-hexene and diphenylacetylene. Although the reasons for this latter observation could not be completely deduced, we suggest that any observable catalysis is likely to be a result of solution dissociation into neutral species and that onward silane metathesis is actually perturbed by the charged constitution of the multimetallic hydride species.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: CCDC 1934906-1934908 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Notes

The authors declare no competing financial interest.

Acknowledgements

The EPSRC (UK) are acknowledged for financial support under awards EP/R020752/1 and EP/N014456/1.

References

1. Harder, S., Molecular early main group metal hydrides: synthetic challenge, structures and applications. *Chem. Commun.* **2012**, 48, 11165-11177.
2. Maitland, B.; Wiesinger, M.; Langer, J.; Ballmann, G.; Pahl, J.; Elsen, H.; Farber, C.; Harder, S., A Simple Route to Calcium and Strontium Hydride Clusters. *Angew. Chem. Int. Ed.* **2017**, 56, 11880-11884.
3. de Bruin-Dickason, C. N.; Sutcliffe, T.; Lamsfus, C. A.; Deacon, G. B.; Maron, L.; Jones, C., Kinetic stabilisation of a molecular strontium hydride complex using an extremely bulky amidinate ligand. *Chem. Commun.* **2018**, 54, 786-789.
4. Harder, S.; Rösch, B.; Xaver Gentner, T.; Elsen, H.; Langer, J.; Wiesinger, M., Nucleophilic aromatic substitution at benzene with powerful strontium hydride and alkyl complexes. *Angew. Chem. Int. Ed.* **2019**, 58, 5396-5401.
5. Shi, X. H.; Hou, C. P.; Zhou, C. L.; Song, Y. Y.; Cheng, J. H., A Molecular Barium Hydrido Complex Stabilized by a Super-Bulky Hydrotris(pyrazolyl)borate Ligand. *Angew. Chem. Int. Ed.* **2017**, 56, 16650-16653.
6. Wiesinger, M.; Maitland, B.; Farber, C.; Ballmann, G.; Fischer, C.; Elsen, H.; Harder, S., Simple Access to the Heaviest Alkaline Earth Metal Hydride: A Strongly Reducing Hydrocarbon-Soluble Barium Hydride Cluster. *Angew. Chem. Int. Ed.* **2017**, 56, 16654-16659.
7. Mukherjee, D.; Okuda, J., Molecular Magnesium Hydrides. *Angew. Chem. Int. Ed.* **2018**, 57, 1458-1473.
8. Mukherjee, D.; Schuhknecht, D.; Okuda, J., Hydrido Complexes of Calcium: A New Family of Molecular Alkaline-Earth-Metal Compounds. *Angew. Chem. Int. Ed.* **2018**, 57, 9590-9602.
9. Green, S. P.; Jones, C.; Stasch, A., Stable Adducts of a Dimeric Magnesium(I) Compound. *Angew. Chem. Int. Ed.* **2008**, 47, 9079-9083.
10. Harder, S.; Brettar, J., Rational design of a well-defined soluble calcium hydride complex. *Angew. Chem. Int. Ed.* **2006**, 45, 3474-3478.
11. Ruspica, C.; Nembenna, S.; Hofmeister, A.; Magull, J.; Harder, S.; Roesky, H. W., A well-defined hydrocarbon-soluble calcium hydroxide: Synthesis, structure and reactivity. *J. Am. Chem. Soc.* **2006**, 128, 15000-15004.
12. Ruspica, C.; Harder, S., Big ligands for stabilization of small functionalities in calcium chemistry. *Inorg. Chem.* **2007**, 46, 10426-10433.
13. Jochmann, P.; Davin, J. P.; Spaniol, T. P.; Maron, L.; Okuda, J., A Cationic Calcium Hydride Cluster Stabilized by Cyclen-Derived Macrocyclic N,N,N,N Ligands. *Angew. Chem. Int. Ed.* **2012**, 51, 4452-4455.

14. Leich, V.; Spaniol, T. P.; Okuda, J., Formation of a Cationic Calcium Hydride Cluster with a "Naked" Triphenylsilyl Anion by Hydrogenolysis of Bis(triphenylsilyl)calcium. *Inorg. Chem.* **2015**, *54*, 4927-4933.
15. Leich, V.; Spaniol, T. P.; Maron, L.; Okuda, J., Molecular Calcium Hydride: Dicalcium Trihydride Cation Stabilized by a Neutral NNNN-Type Macrocyclic Ligand. *Angew. Chem. Int. Ed.* **2016**, *55*, 4794-4797.
16. Causero, A.; Ballmann, G.; Pahl, J.; Zijlstra, H.; Farber, C.; Harder, S., Stabilization of Calcium Hydride Complexes by Fine Tuning of Amidinate Ligands. *Organometallics* **2016**, *35*, 3350-3360.
17. Causero, A.; Ballmann, G.; Pahl, J.; Farber, C.; Intemann, J.; Harder, S., β -Diketiminato calcium hydride complexes: the importance of solvent effects. *Dalton Trans.* **2017**, *46*, 1822-1831.
18. Wilson, A. S. S.; Hill, M. S.; Mahon, M. F.; Dinoi, C.; Maron, L., Organocalcium-mediated nucleophilic alkylation of benzene. *Science* **2017**, *358*, 1168-1171.
19. Bauer, H.; Alonso, M.; Farber, C.; Elsen, H.; Pahl, J.; Causero, A.; Ballmann, G.; De Proft, F.; Harder, S., Imine hydrogenation with simple alkaline earth metal catalysts. *Nature Catalysis* **2018**, *1*, 40-47.
20. Intemann, J.; Bauer, H.; Pahl, J.; Maron, L.; Harder, S., Calcium Hydride Catalyzed Highly 1,2-Selective Pyridine Hydrosilylation. *Chem. Eur. J.* **2015**, *21*, 11452-11461.
21. Bauer, H.; Thum, K.; Alonso, M.; Fischer, C.; Harder, S., Alkene Transfer Hydrogenation with Alkaline-Earth Metal Catalysts. *Angew. Chem. Int. Ed.* **2019**, *58*, 4248-4253.
22. Arrowsmith, M.; Hill, M. S.; MacDougall, D. J.; Mahon, M. F., A Hydride-Rich Magnesium Cluster. *Angew. Chem. Int. Ed.* **2009**, *48*, 4013-4016.
23. Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J., β -Diketiminato-Stabilized Magnesium(I) Dimers and Magnesium(II) Hydride Complexes: Synthesis, Characterization, Adduct Formation, and Reactivity Studies. *Chem. Eur. J.* **2010**, *16*, 938-955.
24. Fohlmeister, L.; Stasch, A., Ring-Shaped Phosphinoamido-Magnesium-Hydride Complexes: Syntheses, Structures, Reactivity and Catalysis. *Chem. Eur. J.* **2016**, *22*, 10235-10246.
25. Liptrot, D. J.; Hill, M. S.; Mahon, M. F., Heterobimetallic s-Block Hydrides by sigma-Bond Metathesis. *Chem. Eur. J.* **2014**, *20*, 9871-9874.
26. Langer, J.; Kosygin, I.; Puchta, R.; Pahl, J.; Harder, S., A Soft Grip: Magnesium Complexes with a Phosphine-Modified Phosphonium Diylidic Lewis Base. *Chem. Eur. J.* **2016**, *22*, 17425-17435.
27. Andrikopoulos, P. C.; Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B., Synthesis, structure and theoretical studies of the hydrido inverse crown $K_2Mg_2(NiPr_2)_4(\mu-H)_2(toluene)_2$: a rare example of a molecular magnesium hydride with a $Mg-(\mu-H)_2-Mg$ double bridge. *Eur. J. Inorg. Chem.* **2003**, 3354-3362.

28. Arrowsmith, M.; Maitland, B.; Kociok-Köhn, G.; Stasch, A.; Jones, C.; Hill, M. S., Mononuclear Three-Coordinate Magnesium Complexes of a Highly Sterically Encumbered beta-Diketiminato Ligand. *Inorg. Chem.* **2014**, *53*, 10543-10552.
29. Harder, S.; Spielmann, J.; Intemann, J., Synthesis and thermal decomposition of a pyridylene-bridged bis- β -diketiminato magnesium hydride cluster. *Dalton Trans.* **2014**, *43*, 14284-14290.
30. Harder, S.; Spielmann, J.; Intemann, J.; Bandmann, H., Hydrogen Storage in Magnesium Hydride: The Molecular Approach. *Angew. Chem. Int. Ed.* **2011**, *50*, 4156-4160.
31. Martin, D.; Beckerle, K.; Schnitzler, S.; Spaniol, T. P.; Maron, L.; Okuda, J., Discrete Magnesium Hydride Aggregates: A Cationic $\text{Mg}_{13}\text{H}_{18}$ Cluster Stabilized by NNNN-Type Macrocycles. *Angew. Chem. Int. Ed.* **2015**, *54*, 4115-4118.
32. Rauch, M.; Ruccolo, S.; Parkin, G., Synthesis, Structure, and Reactivity of a Terminal Magnesium Hydride Compound with a Carbatrane Motif, $\text{Tism}(\text{PriBenz}) \text{MgH}$: A Multifunctional Catalyst for Hydrosilylation and Hydroboration. *J. Am. Chem. Soc.* **2017**, *139*, 13264-13267.
33. Banerjee, S.; Ankur; Andrews, A.; Venugopal, A., A disguised hydride in a butylmagnesium cation. *Chem. Commun.* **2018**, *54*, 5788-5791.
34. Lemmerz, L. E.; Mukherjee, D.; Spaniol, T. P.; Wong, A.; Menard, G.; Maron, L.; Okuda, J., Cationic magnesium hydride MgH^+ stabilized by an NNNN-type macrocycle. *Chem. Commun.* **2019**, *55*, 3199-3202.
35. Schnitzler, S.; Spaniol, T. P.; Okuda, J., Reactivity of a Molecular Magnesium Hydride Featuring a Terminal Magnesium-Hydrogen Bond. *Inorg. Chem.* **2016**, *55*, 12997-13006.
36. Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Procopiou, P. A., Heterofunctionalization catalysis with organometallic complexes of calcium, strontium and barium. *Proc. Roy. Soc. a-Math. Phys. Eng. Sci.* **2010**, *466*, 927-963.
37. Crimmin, M. R.; Hill, M. S., Homogeneous Catalysis with Organometallic Complexes of Group 2. *Alkaline-Earth Metal Compounds: Oddities and Applications*, Harder, S., Ed. 2013; Vol. 45, pp 191-241.
38. Harder, S., From Limestone to Catalysis: Application of Calcium Compounds as Homogeneous Catalysts. *Chem. Rev.* **2010**, *110*, 3852-3876.
39. Hill, M. S.; Liptrot, D. J.; Weetman, C., Alkaline earths as main group reagents in molecular catalysis. *Chem. Soc. Rev.* **2016**, *45*, 972-988.
40. Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Kohn, G., Magnesium-catalysed hydroboration of aldehydes and ketones. *Chem. Commun.* **2012**, *48*, 4567-4569.
41. Yang, Y.; Anker, M. D.; Fang, J.; Mahon, M. F.; Maron, L.; Weetman, C.; Hill, M. S., Hydrodeoxygenation of isocyanates: snapshots of a magnesium-mediated C=O bond cleavage. *Chem. Sci.* **2017**, *8*, 3529-3537.
42. Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C., Magnesium-Catalyzed Hydroboration of Pyridines. *Organometallics* **2011**, *30*, 5556-5559.

43. Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G., Magnesium Catalysis of Imine Hydroboration. *Chem. Eur. J.* **2013**, *19*, 2776-2783.
44. Weetman, C.; Hill, M. S.; Mahon, M. F., Magnesium-catalysed hydroboration of pyridines: Kinetic analysis and poly-pyridine dearomatisation. *Polyhedron* **2016**, *103*, 115-120.
45. Weetman, C.; Hill, M. S.; Mahon, M. F., Magnesium Catalysis for the Hydroboration of Carbodiimides. *Chem. Eur. J.* **2016**, *22*, 7158-7162.
46. Anker, M. D.; Hill, M. S.; Lowe, J. P.; Mahon, M. F., Alkaline-Earth-Promoted CO Homologation and Reductive Catalysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 10009-10011.
47. Anker, M. D.; Kefalidis, C. E.; Yang, Y.; Fang, J.; Hill, M. S.; Mahon, M. F.; Maron, L., Alkaline Earth-Centered CO Homologation, Reduction and Amine Carbonylation. *J. Am. Chem. Soc.* **2017**, *139*, 10036-10054.
48. Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Kohn, G.; Liptrot, D. J.; Mahon, M. F., Magnesium-catalysed nitrile hydroboration. *Chem. Sci.* **2016**, *7*, 628-641.
49. Weetman, C.; Hill, M. S.; Mahon, M. F., Magnesium-catalysed hydroboration of isonitriles. *Chem. Commun.* **2015**, *51*, 14477-14480.
50. (a) Ashby, E. C.; Smith, T., Hydrometallation of alkenes and alkynes with magnesium hydride. *J. Chem. Soc. Chem. Commun.* **1978**, 30-31; (b) Ashby, E. C.; Ainslie, R. D., Hydrometallation of 1-octene with Grignard reagents and alkylmagnesium hydrides catalyzed by dicyclopentadienyltitanium dichloride. *J. Organometal. Chem.* **1983**, *250*, 1-12.
51. (a) Bogdanovic, B.; Maruthamuthu, M., The catalyzed addition of magnesium hydride to isoprene and styrene. *J. Organometal. Chem.* **1984**, *272*, 115-122; (b) Bogdanovic, B., Catalytic synthesis of organolithium and organomagnesium compounds and of lithium and magnesium hydrides – applications in organic synthesis and hydrogen storage. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 262-273; (c) Bogdanovic, B.; Bons, P.; Konstantinovic, S.; Schwickardi, M.; Westeppe, U., Diorganomagnesium compounds from magnesium, hydrogen and 1-alkenes and their application in synthesis.. *Chem. Ber. Rec.* **1993**, *126*, 1371-1383.
52. Ilies, L.; Yoshida, T.; Nakamura, E., Iron-Catalyzed Chemo- and Stereoselective Hydromagnesiation of Diarylalkynes and Diynes. *J. Am. Chem. Soc.* **2012**, *134*, 16951–16954.
53. (a) Greenhalgh, M. D.; Thomas, S. P., Iron-Catalyzed Hydromagnesiation of Olefins. *Synlett*, **2013**, *24*, 0531–0534; (b) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P., Iron-Catalysed Hydrofunctionalisation of Alkenes and Alkynes. *ChemCatChem* **2015**, *7*, 190–222.
54. (a) Jones, A. S.; Paliga, J. F.; Greenhalgh, M. D.; Quibell, J. M.; Steven, A.; Thomas, S. P., Broad Scope Hydrofunctionalization of Styrene Derivatives Using Iron-Catalyzed Hydromagnesiation. *Org. Lett.* **2014**, *16*, 5964–5967; (b) Greenhalgh, M. D.; Kolodziej, A.; Sinclair, F.; Thomas, S. P. Iron-Catalyzed Hydromagnesiation: Synthesis and Characterization of Benzylic Grignard Reagent Intermediate and Application in the Synthesis of Ibuprofen. *Organometallics* **2014**, *33*, 5811–5819; (c) Neate, P. G. N.; Greenhalgh, M. D.; Brennessel, W. W.; Thomas, S. P.; Neidig,

- M. L., Mechanism of the Bis(imino)pyridine-Iron-Catalyzed Hydromagnesiation of Styrene Derivatives. *J. Am. Chem. Soc.* **2019**, *141*, 10099-10108.
55. Garcia, L.; Mahon, M. F.; Hill, M. S., Magnesium hydride alkene insertion and catalytic hydrosilylation. *Chem. Sci.* **2019**, accepted article, DOI: 10.1039/C9SC02056J.
 56. Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Kohn, G.; Liptrot, D. J.; Mahon, M. F.; Weetman, C., Selective reduction of CO₂ to a methanol equivalent by B(C₆F₅)₃-activated alkaline earth catalysis. *Chem. Sci.* **2014**, *5*, 2826-2830.
 57. Anker, M. D.; Arrowsmith, M.; Arrowsmith, R. L.; Hill, M. S.; Mahon, M. F., Alkaline-Earth Derivatives of the Reactive HB(C₆F₅)₃⁻ Anion. *Inorg. Chem.* **2017**, *56*, 5976-5983.
 58. Garcia, L.; Anker, M. D.; Mahon, M. F.; Maron, L.; Hill, M. S., Coordination of arenes and phosphines by charge separated alkaline earth cations. *Dalton Trans.* **2018**, *47*, 12684-12693.
 59. Pahl, J.; Brand, S.; Elsen, H.; Harder, S., Highly Lewis acidic cationic alkaline earth metal complexes. *Chem. Commun.* **2018**, *54*, 8685-8688.
 60. Pahl, J.; Friedrich, A.; Eisen, H.; Harder, S., Cationic Magnesium pi-Arene Complexes. *Organometallics* **2018**, *37*, 2901-2909.
 61. Pahl, J.; Elsen, H.; Friedrich, A.; Harder, S., Unsupported metal silyl ether coordination. *Chem. Commun.* **2018**, *54*, 7846-7849.
 62. Pahl, J.; Stennett, T. E.; Volland, M.; Guldi, D. M.; Harder, S., Complexation and Versatile Reactivity of a Highly Lewis Acidic Cationic Mg Complex with Alkynes and Phosphines. *Chem. Eur. J.* **2019**, *25*, 2025-2034.
 63. Atwood, J. L.; Atwood, J. D., Nonstoichiometric liquid enclosure compounds (liquid clathrates). *Adv. in Chem. Ser.* **1976**, 112-127.
 64. Hill, M. S.; Kociok-Köhn, G.; MacDougall, D. J., N-Heterocyclic Carbenes and Charge Separation in Heterometallic s-Block Silylamides. *Inorg. Chem.* **2011**, *50*, 5234-5241.
 65. Gallagher, D. J.; Henderson, K. W.; Kennedy, A. R.; O'Hara, C. T.; Mulvey, R. E.; Rowlings, R. B., Hydride encapsulation in s-block metal inverse crown chemistry. *Chem. Commun.* **2002**, 376-377.
 66. Graham, D. V.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T., A polymeric solvent-free variant of a hydridomagnesium inverse crown. *Acta Cryst. C Cryst. Struct. Commun.* **2006**, *62*, M366-M368.
 67. Kaupp, M., "Non-VSEPR" structures and bonding in d⁰ systems. *Angew. Chem. Int. Ed.* **2001**, *40*, 3534-3565.
 68. Seyferth, D.; Pudvin, J. J., The generation of a highly reactive intermediate in the high temperature pyrolysis of tetramethylsilane. *Chemtech* **1981**, *11*, 230-233.
 69. Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B., Kinetic stability of heteroleptic (beta-diketiminato) heavier alkaline-earth (Ca, Sr, Ba) amides. *Dalton Trans.* **2005**, 278-284.
 70. Harder, S., Homoleptic beta-diketiminato complexes of the alkaline-earth metals: Trends in the series Mg, Ca, Sr, and Ba. *Organometallics* **2002**, *21*, 3782-3787.

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